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# ***On Certain Applications of the Theory of Probability to Physical Phenomena.***

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Since the discovery of the Principle of Conservation of Energy, it has been one of the chief objects of Mathematical Physics to account for all physical phenomena as far as possible by means of the principles of Theoretical Dynamics. The main difficulty in doing so arises from the fact that the equations of motion of an ideal system always represent perfectly reversible motions, whereas in the phenomena of nature reversible processes are conspicuous by their absence. To account for the Second Law of Thermodynamics, as applied to irreversible transformations, something is needed besides the ordinary equations of dynamics, and the Theory of Probability suggests one possible way out of the difficulty.

According to the Kinetic Theory, the molecules of a gas are always moving about freely in all directions, and when they come within a certain distance apart, they repel each other and rebound in the same way that perfectly elastic bodies would do after a collision. As Lord Salisbury has said, "What the atom of each element is, whether it is a movement or a thing or a vortex or a point having inertia . . . . all these questions remain surrounded by a darkness as profound as ever." But whatever be the correct answer to these unsolved enigmas, it is remarkable that determinations of the ratios of the specific heats of gases accord on the whole very fairly closely with the theory according to which the molecules of gases can, so far as thermal phenomena are concerned, be represented by rigid bodies, whose energy is in most cases partly translational and rotational. The new gas Argon discovered by Lord Rayleigh and Professor Ramsay is peculiar in being the only gas besides mercury-vapor in which the energy is purely translational.

Corresponding to the property that the entropy of a system of unequally heated bodies always tends to a maximum, it has been established by Boltzmann

that when a medium consisting of gas-molecules has been disturbed and is left to itself, a certain function tends to a minimum, and this minimum value is attained when the motions are distributed according to the well-known Boltzmann-Maxwell Law.

Now it has been objected, in the course of a controversy in *Nature*, that if the velocities of every molecule were all exactly reversed, the system would exactly retrace its steps, so that the function in question would increase instead of decreasing; and it has further been suggested that since the number of direct motions is necessarily equal to the number of reverse motions, the chances are just as great that the function increases as that it decreases. The fallacy of this argument lies in the fact that the probability of an event depends not only on the number of ways in which it can happen, but also quite as much on the number of ways in which it can fail. And if this is greater for the reversed than for the direct motion, we may safely infer that in the ordinary course of events there will be a preponderance of direct over reverse motions.

Thus if a number of bodies have been projected from a common point in different directions, it is theoretically possible to imagine their motions at any instant reversed, so that they all return to the point of projection, but if we were to attempt to throw them back we should find it practically impossible to bring them together again, because the chances of our failing would be so overwhelmingly great.

In the problem considered by Boltzmann, a number of molecules of gas are supposed to start with their motions distributed according to a law different to that which they have in their equilibrium state, such initial distribution being presumably the result of an artificially produced disturbance. For example, the gas may have been unequally heated, or two portions of it at different pressures may have been allowed to mix. Because the molecules tend to assume their equilibrium distribution, it is none the more probable that if left to themselves they will ever tend to return to their initial state, as the odds are overwhelmingly against their doing so as a matter of pure chance. In the direct motion the number of ways that the molecules can move is limited by the initial conditions, in the reversed motion it is limited by the final conditions. Hence, in order to prove that there is in general a tendency among the molecules of a gas to assume the Boltzmann-Maxwell distribution, it is sufficient to show that the number of ways in which the molecules can move consistently with this distribution is greater than the number of ways in which they could move if their motions

were distributed in any other arbitrary manner. The following solution of this problem is due to Boltzmann, whose original investigations are, however, very lengthy.

CASE I.—Let there be a finite though large number ( $n$ ) of molecules, and suppose that the kinetic energy of each molecule must have one or other of a discrete series of values  $e, 2e, 3e, \dots pe$ . Taking the total energy  $T$  of the system as equal to  $\lambda e$ , let us investigate the probability that it should be divided between the molecules in a given manner, each value of the energy being *a priori* equally probable for any single molecule. If  $w_0, w_1, w_2, \dots w_p$  be the numbers of molecules having energies  $0, e, 2e, \dots pe$ , the number of permutations of the molecules satisfying this distribution will be

$$P = \frac{n!}{w_0! w_1! \dots w_p!}, \quad (1)$$

where  $w_0, w_1, w_2, \dots w_p$  are subject to the conditions

$$w_0 + w_1 + \dots + w_p = n, \quad (2)$$

$$w_1 + 2w_2 + \dots + pw_p = \lambda. \quad (3)$$

The most probable distribution is that in which the number of permutations is greatest. Let  $H$  denote the logarithm of the denominator of  $P$ , that is, let

$$H = \log(w_0!) + \log(w_1!) + \dots \quad (4)$$

We have therefore to make  $H$  a minimum subject to the conditions (2), (3). Now when  $n$  is very great,  $w!$  may be replaced by its approximate value

$$\sqrt{(2\pi)} \left( \frac{w}{\varepsilon} \right)^w, \quad (5)$$

where  $\varepsilon$  is the base of the Napierian logarithms; therefore by substitution

$$H = \frac{1}{2} \log 2\pi + \sum_{i=0}^{i=p} w_i (\log w_i - 1).$$

Passing to the limiting case in which the energy is capable of continuous variation, let  $f(x) dx$  denote the number of molecules whose energy is between  $x$  and  $x + dx$ . Then we may put

$$w_0 = ef(0), \quad w_1 = ef(e) \dots w_p = ef(pe), \quad (6)$$

where  $e = dx$  in the limit. Hence the problem reduces to finding the minimum of

$$H = \int_0^\infty f(x) \{ \log f(x) - 1 \} dx, \quad (7)$$

subject to the conditions

$$n = \int_0^{\infty} f(x) dx, \quad (8)$$

$$T = \int_0^{\infty} x f(x) dx. \quad (9)$$

The solution is

$$f(x) dx = C e^{-hx} dx. \quad (10)$$

This therefore is the most probable distribution of the energy among the molecules on the hypothesis that all values of the energy are *a priori* equally probable for any one molecule. If  $m$  is the mass of a molecule, the most probable number of molecules with velocities between  $v$  and  $v + dv$  is

$$C e^{-\frac{1}{2} h m v^2} m v dv. \quad (11)$$

This is the Boltzmann-Maxwell distribution of speed for a system of monatomic molecules *moving in one plane*.

CASE II.—To obtain the Boltzmann-Maxwell distribution for molecules moving in three dimensions, it is necessary to make a different assumption with regard to the *a priori* probabilities for the individual molecules. We therefore assume that if  $u, v, w$  be the velocity components of a molecule along the axes of coordinates, all values of  $u, v, w$  are *a priori* equally probable.

The problem of determining the most probable distribution now reduces to finding the minimum of  $H$  where

$$H = \iiint \{f \log f - 1\} du dv dw, \quad (12)$$

subject to the conditions

$$n = \iiint f du dv dw, \quad (13)$$

$$T = \frac{1}{2} m \iiint (u^2 + v^2 + w^2) du dv dw. \quad (14)$$

CASE III.—Let the gas consist of molecules moving about freely or in a field of external force, each molecule having  $r$  degrees of freedom and its motion being specified by the generalized coordinates  $q_1, q_2, \dots, q_r$  and the corresponding generalized momenta,  $p_1, p_2, \dots, p_r$ . Then it has been shown (see Watson, "Kinetic Theory of Gases") that throughout the motion of a molecule the multiple differential

$$dp_1 \cdot dp_2 \cdot \dots \cdot dp_r \cdot dq_1 \cdot dq_2 \cdot \dots \cdot dq_r$$

is constant. We are therefore justified in assuming that the *a priori* probability that the coordinates and momenta of a molecule lie between the limits of this multiple differential is independent of the actual values of the coordinates and momenta. As Boltzmann puts it, we may suppose an urn filled with tickets, each ticket inscribed with a set of values of  $p_1, p_2, \dots, q_r$ , the number of tickets in which the values in question lie between the limits  $dp_1, \dots, dq_r$  being measured by the product of the multiple differential  $dp_1, \dots, dq_r$  into a constant. In the case of a mixture of gases, there would have to be a number of urns equal to the number of gases, and the number of tickets drawn from each urn would have to equal the number of molecules of the gas in question in the mixture. We suppose that a drawing from the various urns has been made, and that the energy of the assemblage of molecules represented by the selected tickets is known, and the problem is to find what is *a posteriori* the most probable distribution of the values of  $p_1, p_2, \dots, q_r$  consistent with this energy condition. [The terms *a priori* and *a posteriori* probability are defined in any text-book on algebra.]

The final result is that if  $f(p_1, \dots, q_r) dp_1, \dots, dq_r$  denote the number of molecules whose coordinates and momenta lie within the limits of the multiple differential, then the most probable distribution is found by making  $H$  a minimum, where

$$H = \sum \{ f \log f - 1 \} dp_1, \dots, dq_r, \quad (15)$$

and the sign of summation  $\sum$  refers to the different kinds of molecules when a mixture of several gases is considered.

The expression  $H$  is in every case *Boltzmann's minimum function*.

CASE IV.—The particular assumption as to the law of *a priori* probability precludes the above investigations from furnishing a complete proof of the Boltzmann-Maxwell Law. In a subsequent paper Boltzmann has removed this restriction and has considered the *a posteriori* probabilities corresponding to any assumed law of *a priori* probability. In other words, we start with a large number ( $N$ ) of molecules having a given distribution of energy, and from them a smaller number ( $n$ ) are selected, and their mean energy is found to have a certain value which may be either the same or different from that of the original  $N$ . It is required to find the most probable law of distribution in the  $n$  selected molecules, or generally the probability of any given distribution.

Boltzmann first considers the case where the original molecules follow the Boltzmann-Maxwell Law for two-dimensional space and points out the necessary modifications for space of three dimensions. In the general case, supposing  $f_1, f_2, \dots, f_p$  to denote the *a priori* probabilities of a molecule having energies  $e, 2e, \dots, pe$ , the *a posteriori* probability of a combination in which the numbers of molecules having these energies are  $w_0, w_1, \dots, w_p$  is proportional to  $\Omega$  where

$$\Omega = f_0^{w_0} f_1^{w_1} \dots f_p^{w_p} \frac{n!}{w_0! w_1! w_2! \dots}, \quad (16)$$

where as before

$$\sum w_i = n, \quad \sum i w_i = \lambda.$$

The approximate expression for  $w!$  now gives

$$\log \Omega = \sum w_i \log f_i - \sum w_i \log w_i + \text{const.},$$

and Boltzmann finds the following results:

If the mean energy of the selected  $n$  molecules is equal to the mean energy of the original  $N$ , the most probable distribution of energy in the latter is identical with the distribution in the former.

If, however, the mean energy of the smaller number is unequal to that of the larger, the most probable distribution is that given by the form

$$w_k = \frac{an}{N} f_k e^{hke}. \quad (17)$$

It thus appears that even the Theory of Probability does not furnish us with a *conclusive* proof of the Boltzmann-Maxwell Law. That the law in question represents accurately the state of the molecules in a perfect gas, and approximately their state in an ordinary gas, cannot be doubted, but directly we attempt to generalize the law by applying it to assemblages of densely crowded molecules we are confronted with the necessity of making some assumption or other, and the above treatment shows that even probability considerations do not afford a sure way out of the difficulty.